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Patent Abstracts of Japan

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TITLE : COLORING ANODIC OXIDATION TREATMENT BATH AND METHOD OF ALUMINUM OR ALUMINUM ALLOY

ABSTRACT : PURPOSE: To obtain a colored film with excellent adhesiveness and reproducibility by adding a fatty acid or either one of aromatic mono- or poly-carboxylic acid having a predetermined number of carbons to the coloring anodic oxidation treatment bath containing an alkane sulfonic acid and a metal salt thereof.

CONSTITUTION: An electrolytic bath containing an alkane sulfonic acid shown by a general formula  $R_1-SO_3H$  or a hydroxyl group containing alkane sulfonic acid shown by a general formula  $HO-R_2-SO_3H$  and either one of metal salts of two kinds of the above described acids is prepared and, further, 1-12C fatty acid or either one of 6-12C aromatic mono- or poly-carboxylic acid is added thereto. In the resulting electrolytic bath, pretreated Al or Al alloy is immersed to carry out electrolysis.

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Japanese Unexamined Patent Application Laid Open 59-152960

[Translator's Note: An amendment of the office file number in accordance with the regulations of Article 17 - 2 of the Patent Law, and a procedural amendment by the applicant dated January 19 1988 and which was published on April 20, 1988, is attached to the end of the Japanese text, and the amended section headed "Scope of the Patent Claims" noted therein has been incorporated into this translation, but claim 5, which is not included in the amended claims, has also been reproduced from the section "Scope of the Patent Claims" in the original text before amendment.]

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10 (54) A coloring anodic oxidation treatment bath, and a method of treatment, for aluminum or aluminum alloys

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## SPECIFICATION

### 1. Title of the Invention

A coloring anodic oxidation treatment bath, and a method of treatment,  
for aluminum or aluminum alloys

### 2. Scope of the Patent Claims

#### We claim:

1. A coloring anodic oxidation treatment bath for aluminum or aluminum alloys, which contains an alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid and a metal salt of an alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid, to which a carboxyl group containing compound has been added.
2. The treatment bath claimed in claim 1, wherein the carboxyl group containing compound is an aliphatic mono-carboxylic acid which has from 1 to 12 carbon atoms or an aromatic mono-carboxylic acid which has from 6 to 12 carbon atoms.
3. The treatment bath claimed in claim 1, wherein the carboxyl group containing compound is an aliphatic poly-carboxylic acid which has from 1 to 12 carbon atoms or an aromatic poly-carboxylic acid which has from 6 to 12 carbon atoms.
4. The treatment bath claimed in claim 1, 2 or 3, wherein the carboxyl group containing compound contains one or more hydroxyl group or sulfonic acid group.
5. A method for the coloring anodic oxidation treatment of aluminum or aluminum alloys wherein the aluminum or aluminum alloy is subjected to an anodic oxidation treatment and then electrolysis is carried out in a treatment bath as claimed in any of claims 1 to 4.

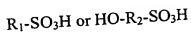
### 3. Detailed Description of the Invention

The invention concerns a coloring anodic oxidation treatment bath, and a method of treatment, for aluminum or aluminum alloys, and in particular it concerns ideal baths and method for use in a coloring anodic oxidation treatment which involves a secondary electrolysis method.

Conventionally, methods of coloring with organic paints and with the AC electrolysis method where inorganic metal salt coloring or natural coloring of an aluminum alloy is achieved by electrolysis in an organic acid bath have been used as methods for the coloring of aluminum.

However, the coloring obtained with paints has poor weather resistance and poor heat resistance, and with the natural coloring methods using organic acids the uniformity of the color is uneven and there is a disadvantage in that various color tones cannot be obtained. On the other hand these disadvantages are overcome with the AC electrolysis method but then the coloring speed is slow and there is a further disadvantage with even coloring.

The inventors have already proposed a method for coloring the surface of aluminum or aluminum alloy in which aluminum or aluminum alloy which has been subjected to alumite filming is subjected to alternating current electrolysis in a electrolysis bath which contains alkane sulfonic acid, which can be represented by the general formula indicated below, and a metal salt thereof (Japanese Unexamined Patent Application Laid Open 54-29850), or a hydroxyl group containing alkane sulfonic acid, which can be represented by the general formula indicated below, and a metal salt thereof (Japanese Examined Patent Document 55-9477) and precipitating the metal or metal oxide in the oxide film as a means of overcoming these weaknesses of conventionally colored alumite.



(In these formulae,  $R_1$  and  $R_2$  each represent a hydrocarbyl part which has from 1 to 12 carbon atoms).

Subsequently, as a result of further investigation, it has been discovered that by carrying out electrolysis with the addition of a carboxyl group containing compound to an electrolysis bath which contains alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid, and a metal salt thereof, the coloring speed is higher than with the conventional method and a dense coloration can be obtained, the uniformity is improved, and even with a long electrolysis time it is possible to obtain colored skin films with extremely good reproducibility.

Thus, according to the present invention there is provided a colored anodic oxidation treatment bath for aluminum or aluminum alloys, which contains an alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid and a metal salt of an alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid, to which a carboxyl group containing compound has been added, and a method for the coloring anodic oxidation treatment of aluminum or aluminum alloy in which this bath is used as the secondary electrolysis bath.

The alkane sulfonic acid which is the main agent of a treatment bath of this invention is preferably an acid which can be represented by the general formula  $R_1-SO_3H$  (where  $R_1$  represents a hydrocarbyl part which has from 1 to 12 carbon atoms), and examples include methane sulfonic acid, ethane sulfonic acid, propane sulfonic acid, 2-propane sulfonic acid, butane sulfonic acid, heptane sulfonic acid and such like sulfonic acids. Examples of the preferred hydroxyl group containing alkane sulfonic acid can be represented by the general formula  $HO-R_2-SO_3H$  (where  $R_2$  represents a hydrocarbyl part which has from 1 to 12 carbon atoms), and these include isethionic acid, 2-hydroxypropane-1-sulfonic acid, 1-hydroxypropane-2-sulfonic acid, 3-hydroxypropane-1-sulfonic acid, 2-hydroxybutane-1-sulfonic acid, 4-hydroxybutane-1-sulfonic acid, 2-hydroxyheptane-1-sulfonic acid, 2-hydroxyhexane-1-sulfonic acid and such like sulfonic acids.

Furthermore, the salts of acids such as those indicated above with heavy metals such as tin, lead, nickel, copper, iron, silver, chromium, cobalt, manganese, cadmium, titanium, indium and the like are included among the metal salts of the alkane sulfonic acids or hydroxyl group containing alkane sulfonic acids. These may be used individually, or they can be used as mixtures of two or more types. For example, such mixtures include tin-nickel, tin-lead, tin-copper, nickel-copper and tin-nickel-copper mixtures.

Examples of the carboxyl group containing compounds which are the additives in a treatment bath of this invention include aliphatic mono- or di-carboxylic acids which have from 1 to 12 carbon atoms, and preferably from 1 to 6 carbon atoms, and aromatic mono- or di-carboxylic acids which have from 6 to 12 carbon atoms, and preferably from 6 to 10 carbon atoms. These carboxylic acid compounds may contain one, or more than one, hydroxyl group or sulfonic acid group. Examples of carboxyl group containing compounds which can be used include aliphatic mono-carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid and (illegible word) acid, aliphatic poly-carboxylic acids such as malonic acid, glutaric acid, adipic acid and tricarballic acid, oxycarboxylic acids such as glycolic acid, tartronic acid, malic acid, tartaric acid, citric acid, gluconic

acid and lactic acid, aliphatic sulfo-carboxylic acids such as sulfoacetic acid, 2-sulfopropionic acid, 3-sulfopropionic acid, sulfosuccinic acid, sulfomaleic acid, sulfofumaric acid and sulfocitric acid, and aromatic mono-carboxylic acids and poly-carboxylic acids such as benzoic acid, o- or p-toluic acid, ethylbenzoic acid, salicylic acid, phthalic acid, o-, m- or p-sulfobenzoic acid, 4- or 5-sulfosalicylic acid, 4- or 5-sulfophthalic acid and naphthoic acid.

The coloring anodic oxidation treatment baths of the present invention are aqueous solutions, and the alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid is included generally in an amount of from 10 to 300 g/l, and preferably in an amount of from 30 to 80 g/l, and the metal salt of an alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid is included generally in an amount of from 2 to 50 g/l (as metal) and preferably in an amount of from 5 to 20 g/l (as metal). Moreover, the carboxyl group containing compound as the additive of this invention is included generally in an amount of from 1 g/l and preferably in an amount of from 3 to 10 g/l.

To carry out a coloring anodic oxidation treatment using the abovementioned treatment baths of this invention, the aluminum is first of all subjected to the conventional pre-treatment, for example mechanical or chemical polishing, neutral washing or degreasing with an organic solvent, rinsing and drying. Then, the aluminum is subjected to an anodic oxidation treatment in an ordinary sulfuric acid electrolysis bath and, without carrying out a sealing treatment, it is then subjected to a coloring anodic oxidation treatment of this invention and an excellent deep coloration can be obtained.

The electrolysis conditions are bath temperature from 10 to 40°C and preferably from 20 to 25°C, current density from 0.1 to 2 A/dm<sup>2</sup> and preferably from 0.3 to 0.8 A/dm<sup>2</sup>, voltage from 4 to 25 V and preferably from 8 to 18 V and time from 1 to 20 minutes and preferably from 5 to 8 minutes.

When a carboxyl group containing compound is added to a coloring anodic oxidation treatment bath which has alkane sulfonic acid or hydroxyl group containing alkane sulfonic acid and metal salt of said acid as the main components, the coloring speed is higher than with a conventional bath and the uniformity is improved and, even when electrolysis is carried out for a longer period of time, colored skin films can be obtained with extremely good reproducibility and, moreover, the colors obtained using an electrolysis bath of this invention are deeper than those obtained conventionally as is seen by measuring the brightness of the skin film (L-Value: a smaller L-value indicates deeper color) with a colorimeter.

Illustrative examples of the invention are described below, but the



invention is not limited by these illustrative examples.

#### Example 1

Aluminum sheets (5052S) measuring 0.5 x 70 x 170 mm were subjected to the usual pre-treatment and an oxide skin film of thickness about 10  $\mu$  was formed using the sulfuric acid electrolysis method and then rinsed with water, after which the brightness (L-value) of the colored skin films obtained on electrolysis for 8 minutes at an AC voltage of 14V in the electrolysis baths which had the compositions indicated below was measured using a colorimeter.

	Comparative Bath	Bath of this Invention
Tin 2-Hydroxypropane Sulfonate (as $\text{Sn}^{++}$ )	5 g/l	5 g/l
2-Hydroxypropane Sulfonic Acid	35 g/l	35 g/l
3-Sulfopropionic Acid	-	5 g/l
Brightness	13.2	2.5

#### Example 2

The brightness of the colored skin films obtained by forming oxide films of thickness about 10  $\mu$ m, rinsing and carrying out electrolysis for 8 minutes at an AC voltage of 14 V in electrolysis baths which had the compositions indicated below in the same way as in Example 1 were measured using a colorimeter.

	Comparative Bath	Bath of this Invention
Tin Methane Sulfonate (as $\text{Sn}^{++}$ )	5 g/l	5 g/l
Methane Sulfonic Acid	35 g/l	35 g/l
Sulfosuccinic Acid	-	10 g/l
Brightness	12.3	2.2

#### Example 3

The brightness of the colored skin films obtained by forming oxide films of thickness about 10  $\mu$ m, rinsing and carrying out electrolysis for 5 minutes at an AC voltage of 14 V in electrolysis baths which had the compositions indicated below in the same way as in Example 1 were measured using a colorimeter.

	Comparative Bath	Bath of this Invention
Tin Methane Sulfonate (as $\text{Sn}^{++}$ )	5 g/l	5 g/l
Methane Sulfonic Acid	35 g/l	35 g/l
Gluconic Acid	-	10 g/l
Brightness	13.0	10.5

**Example 4**

The brightness of the colored skin films obtained by forming oxide films of thickness about 10  $\mu\text{m}$ , rinsing and carrying out electrolysis for 6 minutes at an AC voltage of 13.5 V in electrolysis baths which had the compositions indicated below in the same way as in Example 1 were measured using a colorimeter.

	Comparative Bath	Bath of this Invention
Tin 2-Hydroxypropane Sulfonate (as $\text{Sn}^{++}$ )	5 g/l	5 g/l
2-Hydroxypropane Sulfonic Acid	30 g/l	50 g/l
Succinic Acid	-	5 g/l
Brightness	13.6	10.2

**Example 5**

The brightness of the colored skin films obtained by forming oxide films of thickness about 10  $\mu\text{m}$ , rinsing and carrying out electrolysis for 8 minutes at an AC voltage of 15 V in electrolysis baths which had the compositions indicated below in the same way as in Example 1 were measured using a colorimeter.

	Comparative Bath	Bath of this Invention
Tin Ethane Sulfonate (as $\text{Sn}^{++}$ )	5 g/l	5 g/l
Ethane Sulfonic Acid	35 g/l	35 g/l
Citric Acid	-	2 g/l
Brightness	12.3	9.6

**Example 6**

The brightness of the colored skin films obtained by forming oxide films of thickness about 10  $\mu\text{m}$ , rinsing and carrying out electrolysis for 8 minutes at an AC voltage of 15 V in electrolysis baths which had the compositions indicated below in the same way as in Example 1 were measured using a colorimeter.

	Comparative Bath	Bath of this Invention
Tin 2-Hydroxypropane Sulfonate (as $\text{Sn}^{++}$ )	3 g/l	3 g/l
Nickel 2-hydroxypropane Sulfonic Acid (as $\text{Ni}^{++}$ )	30 g/l	30 g/l
2-Hydroxypropane Sulfonic Acid	40 g/l	40 g/l
Sulfosalicylic Acid	-	-
Brightness	12.7	2.8

As indicated in the illustrative examples above, all of the skin films obtained from an electrolysis bath which contained a carboxyl group containing

compound which is the additive of the present invention had improved color density under the same electrolysis conditions.

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